

**REMARKS**

Claims 1 to 4 are pending in the application.

The purpose of this amendment is to insert the reference to the parent application of which this is a Section 371 National Phase, place the application headings in appropriate U.S. form, and generally place the specification and claims in appropriate U.S. form. Such amendments are formal in nature and no new matter is added by any of the above amendments. A marked-up copy of the substitute specification is enclosed to reflect these amendments. Entry of this amendment and early examination of this application are respectfully solicited.

Respectfully submitted,

**Hiroaki ABEKAWA, et al.**

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By:

William W. Schwarze

WILLIAM W. SCHWARZE

Registration No. 25,918

AKIN, GUMP, STRAUSS, HAUER & FELD, L.L.P.

One Commerce Square

2005 Market Street - Suite 2200

Philadelphia, PA 19103-7086

Telephone: (215) 965-1200

Direct Dial: (215) 965-1270

Facsimile: (215) 965-1210

E-Mail: wschwarze@akingump.com

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Marked-up Version of Substitute Specification

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DESCRIPTION

TITLE OF THE INVENTION~~METHOD FOR PRODUCING PROPYLENE OXIDE~~

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~~FIELD OF THE INVENTION~~[0001] Method for Producing Propylene OxideCROSS-REFERENCE TO RELATED APPLICATIONS

[0002] This application is a Section 371 of International Application No. PCT/JP03/002288,  
10 filed February 28, 2003, the disclosure of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0003] The present invention relates to a process for producing propylene oxide by carrying out an epoxidation reaction of propylene using hydrogen peroxide. More specifically, the invention relates to a process for efficiently producing propylene oxide by performing the reaction using a  
15 specific crystalline titanosilicate catalyst having an MWW structure in the presence of an organic solvent.

[0004][0005] BACKGROUND ART

[0006] As the process for producing propylene oxide by carrying out an epoxidation reaction  
20 of propylene using hydrogen peroxide, a method of using a TS-1 catalyst (e.g., Japanese Published Examined Application No. 4-5028) is known. The TS-1 catalyst is a crystalline titanosilicate catalyst having MFI structure in accordance with the framework type code of International Zeolite Association (IZA). In addition, when the TS-1 catalyst is used, a methanol solvent is known to be an appropriate solvent (e.g., *Journal of Catalysis* 129, 159, 129:159 (1991)).

25 [0007] Also, as a process for producing propylene oxide by carrying out an epoxidation reaction of propylene with hydrogen peroxide using MWW structure-having crystalline titanosilicate (hereinafter referred to as Ti-MWW) catalyst, there has been a known method that uses a Ti-MWW catalyst, into which titanium (hereinafter referred to as Ti) has been incorporated after crystallization (e.g., U.S. Patent No. 6114551, 6,114,551).

30 [0008] Moreover, as a process for producing propylene oxide by carrying out an epoxidation reaction of propylene with hydrogen peroxide, as a medium, using a Ti-MWW catalyst, into which Ti has been incorporated during crystallization, there has been a known method that produces propylene oxide in a water solvent, that is, in an aqueous hydrogen peroxide solution (*Heisei 12*

*nendo Jisedai Kagaku Process Gijutu Kaihatu Non-halogen Kagaku Process Gijutu Kaihatu Seika Houkokusho*( Report of R&D projects for “Next-generation Chemical Process Technology /Non-halogen Chemical Process Technology” FY2000 Annual Report) 261-268, (FY2001)).

**[0009]** However, in the conventionally known production methods, sufficient catalytic activities have not been attained.

#### ~~DISCLOSURE~~BRIEF SUMMARY OF THE INVENTION

**[0010]** The object of the present invention is to provide a process for efficiently producing propylene oxide, which process is a production process of propylene oxide by epoxidizing propylene with hydrogen peroxide.

**[0011]** Thus, the present invention relates to a method for producing propylene oxide, characterized in that it comprises reacting propylene with hydrogen peroxide in the presence of an organic solvent and a crystalline titanosilicate catalyst that has an MWW structure prepared by incorporating Ti during crystallization.

#### ~~BEST MODE FOR CARRYING OUT~~DETAILED DESCRIPTION OF THE INVENTION

**[0012]** The crystalline titanosilicate catalyst having an MWW structure to be used in the present invention is generally known as the Ti-MWW catalyst named from the framework type code of IZA (International Zeolite Association) or the Ti-MCM-22 catalyst.

**[0013]** A generally employed process for producing the crystalline titanosilicate catalyst having an MWW structure is as follows.

**[0014]** A silicon (hereinafter referred to as Si) compound and a Ti compound are hydrolyzed in the presence of a structure directing agent to prepare a gel. A lamellar precursor of crystalline titanosilicate is prepared from the resultant gel by heating in the presence of water (hydrothermal synthesis method or the like). The crystalline titanosilicate catalyst having an MWW structure is prepared by calcination of the lamellar precursor for crystallization.

**[0015]** Alternatively, the crystalline titanosilicate having an MWW structure can also be prepared by conducting a preparation according to the above-described method using a Si compound, and a compound other than Ti, such as an ~~Aluminum~~aluminum (hereinafter referred to as Al) compound, or a boron compound, to once prepare, as a precursor, a crystalline metallosilicate having an MWW structure, and subsequently substituting the compound, which was incorporated therein in place of Ti, with Ti.

**[0016]** However, since the pore diameter of a micro-pore structure within a particle of the crystalline titanosilicate catalyst is small in the latter case, it is difficult to incorporate Ti by

substitution into the framework within the pore after crystallization. Therefore, in order to incorporate Ti into the framework within the pore by substitution, the layers of the crystal of the crystalline metallosilicate catalyst having an MWW structure once prepared have to be delaminated, thereby collapsing the crystal, and then substituted with Ti, and crystallized again.

5 **[0017]** With respect to the catalyst to be used in the present invention, it is important to incorporate Ti during crystallization. The incorporation of Ti during the crystallization of Ti-MWW catalyst enables the introduction of Ti into the framework of the pore, thereby the Ti-MWW catalyst that has an MWW structure containing Ti, and which Ti is also present in the pore within the particle can be prepared.

10 **[0018]** That is, the term “during crystallization” in the present invention stands for “during crystallization of the Ti-MWW catalyst”, and does not mean during crystallization of a crystalline metallosilicate catalyst having an element other than Ti formed in the course of preparing the catalyst. Therefore, for instance, a catalyst prepared by delaminating the layers of the crystal of the crystalline metallosilicate catalyst having an MWW structure once prepared, thereby collapsing the  
15 crystal, and by subjecting the resulting to substitution with Ti and then crystallization again, is an intended catalyst of the present invention.

**[0019]** Specific examples of the method for preparing the crystalline titanosilicate catalyst that has an MWW structure and contains Ti having been incorporated during crystallization, include the following methods.

20 **[0020]** Namely, a method of hydrothermal synthesis using titanium alkoxide, described in *Chemistry Letters* ~~774, 774~~ (2000), or a method of synthesis using the dry gel conversion method with titanium alkoxide, described in ~~“The Proceedings of the 88th Catalysis Society of Japan (CatSJ) Meeting A” 154, 154~~ (2000) are known. Alternatively, as described in Shokubai (*Catalysts & Catalysis*) ~~44, 6, 468, 44(6):468~~ (2002), the post synthesis process comprising  
25 crystallizing, delaminating layers of the resulting crystals, thereby collapsing the crystal, incorporating Ti and then crystallizing again, is a preferred process of preparation because the incorporation of Ti during crystallization enables the incorporation of Ti inside the pore.

**[0021]** In addition, since a Ti-MWW catalyst prepared by using Al, due to the acidity of the residual Al, possibly promotes consecutive reactions of propylene oxide, a preferred Ti-MWW  
30 catalyst is one prepared without using an Al compound.

**[0022]** It is known from the disclosure of U.S. Patent No. ~~4954325~~ 4,954,325 that the MWW structure of the catalyst can be confirmed by X-ray diffraction analysis. ~~In~~ *Chemical*

*Communication* 897 (2001), the results of X-ray diffraction analyses of the crystalline titanosilicate catalyst having an MWW structure are described. Also, it can be confirmed by using ultraviolet and visible spectral analyses as to whether the catalyst is the crystalline titanosilicate catalyst.

**[0023]** In the present invention, reaction is carried out in the presence of an organic solvent.

5 The organic solvents that may be used include organic compounds such as alcohols (methanol, t-butanol, and the like), ketone compounds (acetone, and the like), ether compounds (1,4-dioxane, and the like), ester compounds (methyl acetate, ethyl acetate, and the like), nitrile compounds (acetonitrile, propionitrile, and the like), hydrocarbons (n-heptane, toluene, and the like), halogenated hydrocarbons (1,2-dichloroethane, and the like), and the like. Preferred organic  
10 solvents are the nitrile compounds. Among the nitrile compounds, preferred is acetonitrile.

**[0024]** The organic solvent used in the present invention can be used in combination with a compound other than the organic solvents as long as it does not adversely affect the effects of the present invention. Examples of the compound other than organic solvents include water and carbon dioxide. The compound other than organic solvents may be combined with the organic  
15 solvent in a liquid state, or combined with the organic solvent in a supercritical state as well.

**[0025]** The ratio of the organic solvent (A) to the compound (B) other than organic solvents ((A)/(B)) is generally 10/90 to 100/0 by weight.

**[0026]** Methods of supplying hydrogen peroxide include a method of supplying a hydrogen peroxide solution prepared in advance, and a method of supplying hydrogen peroxide synthesized in  
20 the reaction system. The methods of synthesizing hydrogen peroxide in the reaction system include a method of synthesizing hydrogen peroxide from hydrogen and oxygen, by using a transition metal catalyst, which synthesizes hydrogen peroxide, such as palladium (Pd) or gold (Au), carried or mixed with Ti-MWW catalyst.

**[0027]** When a hydrogen peroxide solution produced in advance is supplied, the hydrogen  
25 peroxide concentration in the hydrogen peroxide solution is generally from 0.1 to 70% by weight. In addition, examples of the hydrogen peroxide solution include an aqueous hydrogen peroxide solution or a mixture of hydrogen peroxide solution, water, and the organic solvent.

**[0028]** In the present invention, the epoxidation reaction of propylene with hydrogen peroxide is normally performed at a temperature of 0°C to 150°C and normally under a pressure of  
30 0.1 MPa to 20 MPa.

**[0029]** The reaction methods include a fixed bed flow reaction method and a slurry reaction method.

## EXAMPLES

### EXAMPLE 1

**[0030]** A reaction was carried out using a Ti-MWW catalyst having a Ti content of 1.1% by weight as determined by ICP emission spectrometry, prepared according to the method described in *Chemistry Letters* ~~774~~, 774 (2000). A solution ( $\text{H}_2\text{O}_2$ : 5% by weight, water: 47.5% by weight, and acetonitrile: 47.5% by weight) was prepared using ~~an~~ a 60% aqueous  $\text{H}_2\text{O}_2$  solution (product of Mitsubishi Gas Chemical), acetonitrile, and purified water. Twelve-grams of the solution thus prepared and 0.010 g of milled Ti-MWW catalyst was loaded into a 50 ml stainless steel autoclave. Then, the autoclave was transferred onto an ice bath and thereinto was loaded 10 g of liquid propylene. Further, it was pressurized to 2 MPa-G with nitrogen. The reaction was deemed started when 5 minutes passed after the autoclave had been placed in hot water bath maintained at 40°C, the inside temperature reaching about 35°C. One hour after the reaction starting, the autoclave was taken out of the hot water bath and sampling was conducted. The pressure at sampling starting was 3 MPa-G. The analysis was carried out by gas chromatography. As a result, the propylene oxide producing activity per unit catalyst weight was  $0.463 \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ . The propylene oxide selectivity based on propylene was 99.9%.

### EXAMPLE 2

**[0031]** Twelve-grams of the solution prepared by using 0.011 g of the Ti-MWW catalyst used in Example 1, the aqueous  $\text{H}_2\text{O}_2$  solution, acetonitrile and purified water ( $\text{H}_2\text{O}_2$ : 5% by weight, water: 47.5% by weight, acetonitrile: 47.5% by weight) and 10 g of liquefied propylene were loaded into an autoclave as in Example 1. It was pressurized to 1 MPa-G with nitrogen, and a catalyst evaluation test was conducted in a similar manner as that of Example 1 at 70°C using an aluminum block bath in place of a hot water bath. The pressure at sampling starting was 3 MPa-G. As a result, the propylene oxide producing activity per unit catalyst weight was  $0.973 \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ . The propylene oxide selectivity based on propylene was 98.5%.

### EXAMPLE 3

**[0032]** Twelve-grams of the solution prepared by using 0.010 g of the Ti-MWW catalyst used in Example 1, the aqueous  $\text{H}_2\text{O}_2$  solution, acetone and purified water ( $\text{H}_2\text{O}_2$ : 5% by weight, water: 47.5% by weight, acetone: 47.5% by weight) and 10 g of liquefied propylene were loaded into an autoclave as in Example 1. It was pressurized to 2 MPa-G with nitrogen, and a catalyst evaluation test was conducted in a similar manner as that of Example 1 at 40°C using an aluminum block bath in place of a hot water bath. The pressure at sampling starting was 3 MPa-G. As a

result, the propylene oxide producing activity per unit catalyst weight was  $0.230 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ . The propylene oxide selectivity based on propylene was 98.4%.

#### EXAMPLE 4

**[0033]** A reaction was carried out using a Ti-MWW catalyst having a Ti content of 2% by weight as determined by ICP emission spectrometry, prepared in accordance with the method described in Shokubai (*Catalysts & Catalysis*) 44, 6, 468-470, (2002). Using 12 g of the solution prepared by using 0.010 g of the Ti-MWW catalyst, the aqueous  $\text{H}_2\text{O}_2$  solution, acetonitrile and purified water ( $\text{H}_2\text{O}_2$ : 5% by weight, water: 47.5% by weight, acetonitrile: 47.5% by weight) and 10 g of liquefied propylene, a catalyst evaluation test was conducted in the same manner as that of Example 1 at  $40^\circ\text{C}$  using an aluminum block bath in place of a hot water bath. The pressure at sampling starting was 3 MPa-G. As a result, the propylene oxide producing activity per unit catalyst weight was  $0.684 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ . The propylene oxide selectivity based on propylene was 99.4%.

#### EXAMPLE 5

**[0034]** Twelve-grams of the solution prepared by using 0.010 g of the Ti-MWW catalyst used in Example 1, the aqueous  $\text{H}_2\text{O}_2$  solution, acetonitrile and purified water ( $\text{H}_2\text{O}_2$ : 5% by weight, water: 47.5% by weight, acetonitrile: 47.5% by weight) was loaded into a 50 ml stainless steel autoclave. Then, after the air inside the autoclave was replaced by gaseous propylene, the autoclave was transferred onto an aluminum block bath heated in advance to become  $40^\circ\text{C}$ , and agitation was started. Concurrently with agitation starting, supplying gaseous propylene adjusted in advance to 0.7 MPa-G with a pressure reducing valve allowed a reaction to start while maintaining the reaction pressure at 0.7 MPa-G. Three hours after the reaction starting, sampling was carried out. As a result, the propylene oxide producing activity per unit catalyst weight was  $0.270 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ . The propylene oxide selectivity based on propylene was 99.6%.

#### EXAMPLE 6

**[0035]** Twelve-grams of the solution prepared by using 0.010 g of the Ti-MWW catalyst used in Example 1, the aqueous  $\text{H}_2\text{O}_2$  solution, propionitrile and purified water ( $\text{H}_2\text{O}_2$ : 5% by weight, water: 47.5% by weight, propionitrile: 47.5% by weight) and 10 g of liquefied propylene were loaded into an autoclave as in Example 1. It was pressurized to 2 MPa-G with nitrogen, and a catalyst evaluation test was conducted in the same manner as that of Example 1 at  $40^\circ\text{C}$  using an aluminum block bath in place of a hot water bath. The pressure at sampling starting was 3 MPa-G. As a result, the propylene oxide producing activity per unit catalyst weight was  $0.370 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ .

Compounds derived from propylene detected by gas chromatography were only propylene oxide, and by-products such as propylene glycol were not detected.

#### EXAMPLE 7

**[0036]** Twelve-grams of the solution prepared by using 0.010 g of the Ti-MWW catalyst used in Example 1, the aqueous H<sub>2</sub>O<sub>2</sub> solution, 1,2-dichloroethane and purified water (H<sub>2</sub>O<sub>2</sub>: 5% by weight, water: 47.5% by weight, 1,2-dichloroethane: 47.5% by weight) and 10 g of liquefied propylene were loaded into an autoclave as in Example 1. It was pressurized to 2 MPa-G with nitrogen, and a catalyst evaluation test was conducted in the same manner as that of Example 1 at 40°C using an aluminum block bath in place of a hot water bath. The pressure at sampling starting was 3 MPa-G. As a result, the propylene oxide producing activity per unit catalyst weight was 0.273 mol·h<sup>-1</sup>·g<sup>-1</sup>. The propylene oxide selectivity based on propylene was 97.3%.

#### EXAMPLE 8

**[0037]** Twelve-grams of the solution prepared by using 0.010 g of the Ti-MWW catalyst used in Example 1, the aqueous H<sub>2</sub>O<sub>2</sub> solution, toluene and purified water (H<sub>2</sub>O<sub>2</sub>: 5% by weight, water: 47.5% by weight, toluene: 47.5% by weight) and 10 g of liquefied propylene were loaded into an autoclave as in Example 1. It was pressurized to 2 MPa-G with nitrogen, and a catalyst evaluation test was conducted in a similar manner as that of Example 1 at 40°C using an aluminum block bath in place of a hot water bath. The pressure at sampling starting was 3 MPa-G. As a result, the propylene oxide producing activity per unit catalyst weight was 0.290 mol·h<sup>-1</sup>·g<sup>-1</sup>. The propylene oxide selectivity based on propylene was 98.0%.

#### COMPARATIVE EXAMPLE 1

**[0038]** A reaction was carried out in a similar manner as the method of Example 1 with the exception that a TS-1 catalyst having a Ti content of 1.3% by weight as determined by ICP emission spectrometry, prepared in accordance with the method described in *Journal of Catalysis* ~~130~~, ~~130:1~~ (1991) was used and that methanol was used instead of acetonitrile. The propylene oxide producing activity per unit catalyst weight was 0.165 mol·h<sup>-1</sup>·g<sup>-1</sup>. The propylene oxide selectivity based on propylene was 95.8%.

#### COMPARATIVE EXAMPLE 2

**[0039]** A catalyst evaluation test was conducted in a similar manner as that of Example 4 by use of 12 g of the solution prepared by using 0.010 g of the Ti-MWW catalyst used in Example 1, the aqueous H<sub>2</sub>O<sub>2</sub> solution, and purified water (H<sub>2</sub>O<sub>2</sub>: 5% by weight, water: 95% by weight) and gaseous propylene adjusted to 0.7 MPa-G with a pressure reducing valve. As a result of analyzing



the product after three hours from the reaction starting, the propylene oxide producing activity per unit catalyst weight was  $0.057 \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ . The propylene oxide selectivity based on propylene was 86.8%.

#### INDUSTRIAL APPLICATION

5    **[0040]**        As detailed thus far, according to the present invention there can be provided a process for efficiently producing propylene oxide by reacting hydrogen peroxide with propylene in the presence of a crystalline titanosilicate catalyst having an MWW structure and of an organic solvent.

10    **[0041]**        It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

## CLAIMS

### We claim:

1. (Currently amended) ~~1.~~—A method for producing propylene oxide,  
~~characterized in that it comprises~~comprising reacting propylene with hydrogen  
5 ~~peroxide in the presence of an organic solvent and a crystalline titanosilicate catalyst—that,~~  
wherein the catalyst has an MWW structure containing~~containing~~ Ti, the Ti having been  
incorporated during crystallization.

2. ~~2.~~—A(Currently amended)The method according to claim 1, wherein the organic  
solvent is a nitrile compound.

10 3. ~~3.~~—A(Currently amended)The method according to claim 1, wherein the  
crystalline titanosilicate catalyst having an MWW structure is ~~a titanosilicate catalyst~~  
~~having an MWW structure,~~ prepared without using aluminum.

4. ~~4.~~—A(Currently amended)The method according to claim 1, wherein hydrogen  
peroxide used in the reaction is synthesized within the ~~epoxidation-reaction system of~~  
15 ~~propylene is used in the reaction.~~

~~Abstract~~ ABSTRACT OF THE DISCLOSURE

A method is provided for producing propylene oxide, ~~characterized in that~~  
~~it comprises reacting~~ wherein propylene is reacted with hydrogen peroxide in the presence  
of an organic solvent and a crystalline titanosilicate catalyst ~~that has~~ having an MWW structure  
5 containing Ti, the Ti having been incorporated during crystallization.